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Synthesis of GO-ZnO via Impregnation Method for Fluoride Removal in Wastewater

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ABSTRACT

High concentration of fluoride in wastewater discharge from various industries is threatening the environment due to its hazardous effects and properties. This research work aims to develop an efficient adsorbent for fluoride removal in wastewater. Graphite oxide (GO) was impregnated with ZnO nanoparticles as an adsorbent, and the effect of synthesis parameters of GO-ZnO adsorbent for fluoride removal were studied (sonication temperature, synthesis time, and ratio of GO to ZnO). The surface functional groups of these synthesized adsorbents were analyzed by using FTIR. The synthesis parameters that contribute to the highest adsorption capacity and percentage removal are 5:1 ratio of GO-ZnO, 45 ºC of sonication temperature and 60 minutes of synthesis time, respectively. The highest value of adsorption capacity obtained from the fluoride removal is 55.5 mg/g. The functional groups contained in the GO-ZnO adsorbent are hydroxyl group (O-H), C=O group, aromatics group, carboxyl group (C-O), epoxy group and alkoxy group. These functional groups showed significant impact towards fluoride adsorption due to the bonding of fluoride ion to the functional groups.

Keywords: *Fluoride, Graphite Oxide, Zinc Oxide, Adsorption, Wastewater.*

1. INTRODUCTION

Nowadays, domestic, industrial, commercial or agricultural industries are fast developed, resulting in increasing the amount of wastewater produced. Wastewater is known as a liquid that adversely affected the quality of water. Sources that release the wastewater are from various development activities. At high concentrations, fluoride in wastewater could contribute to adverse hazardous effects, which have affected human health and environment [1]. Recently, numerous industries were discovered as sources of fluoride pollution such as chemical, clinical and semiconductor industries. Generally, fluoride is one of the essential elements for human health, which is beneficial, but at a low concentration. However, excess fluoride intake could cause serious diseases, which affected the skeletal tissues (bone and teeth) as well as non-skeletal tissues (brain, liver, kidney, etc.) [1]. The World Health Organization (WHO) has set a maximum permissible limit of fluoride in potable water up to 1.5 mg/L, while Malaysia's Department of Environment (DOE), allows the acceptable amount of fluoride discharge in portable water from industrial effluent up to 2.0 mg/L and 5.0 mg/L for standards A and B, respectively [2].

There are various technologies available to minimize fluoride concentration in industrial wastewater, such as filtration, distillation, hydrolysis and adsorption [3]. Among these

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technologies, adsorption method has been identified as the most efficient and economic for fluoride removal. Adsorption relies upon adsorbate in liquid diffusing to the surface of a solid adsorbent, where they bond with the solid surface or are held there by frail intermolecular forces. Adsorption studies pointed most important characteristics which decided adsorbent suitability for practical application such as adsorption capacity, selectivity for fluoride ions, regenerability, compatibility, particle and pore size, and cost. Many researchers have studied different type of materials as an adsorbent for fluoride removal such as nanoparticles like materials [4], composite forms of adsorbents [5], activated carbon [6], zeolites [7], calcium based material [8], graphite [9], and other low cost adsorbent materials. Different types of adsorbent have their own characteristics such as porosity, pore structure and nature of its adsorbing surfaces.

In this study, graphite is utilized as an adsorbent. Graphite is the element of a few carbon allotropes, while graphite oxide (GO) is a one-atom thick planar sheet of sp2-bonded carbon atoms densely packed in a honeycomb crystal lattice, which has become a rapid growing star among carbon materials [10]. GO is a carbonaceous material that has a high surface area and functional group such as hydroxyl, epoxy and carboxylic acid group [10]. It can be utilized as an adsorbent for efficient removal of different gasses and water pollutant. This is because GO shows high resistance towards corrosive, due to chemical inertness, toughness, impermeability and negative charge. Subsequently, it is also feasible towards strong adsorption of basic chemicals like fluoride and cationic particle through reactive adsorption and ionic binding [8]. Metal oxide (MO) was selected as a catalyst to be modified with GO due to some special characteristics of metal oxides such as having a higher surface area and high adsorption capacities. The addition of metal oxide on GO will increase the capability of GO to adsorb fluoride from wastewater. There are several metal oxides that are normally used with GO such as calcium, carbon, zinc oxide (ZnO) and iron oxide (Fe_2O_3) [8].

From previous research work, the synthesis of aluminium oxide hydroxide with reduced graphene oxide (AlOOH-RGO) resulted in high adsorption capacity (> 20 mg/g) [11]. Hence, it is anticipated to see the modification of GO with ZnO. The ZnO has broad technological applications such as photonic crystals, catalysts, light-emitting diodes, sensors, electroluminescent and photoluminescent materials [5]. ZnO also received immense attention due to its wide band gaps and high exaction binding energy. In this research, the modification of GO with ZnO will be used for fluoride removal, since the adsorbents prepared with ZnO possessed a favorable textural structure as active component which exhibited good activity of removing pollutant. As such, the main objective of this study is to develop an efficient GO adsorbent that is modified with ZnO for fluoride removal in wastewater.

2. RESEARCH MATERIALS AND METHODS

2.1 Chemicals and Materials

In this research, there are several chemicals that have been used for the synthesis of GO/MO for fluoride removal. The chemicals that have been used in this experiment are commercial graphite powder (Sigma-aldrich, 99.99%), concentrated sulphuric acid, H_2SO_4 (Merck, 96%), potassium permanganate, $KMnO_4$ (99 – 100%), sodium nitrate, $NaNO_3$ (Merck 99 – 100%), hydrogen peroxide, H_2O_2, (Sigma-aldrich, 99%), ammonia, NH_3 (Merck, 95%) and zinc oxide, ZnO (Sigma-aldrich, 98%).

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2.2 Preparation of Graphite Oxide

Graphite oxide (GO) has been synthesized by the oxidation of graphite using modified Hummers method [9]. A 2.5 g of graphite powder was stirred in 60 ml of concentrated H_2SO_4 and after that, a 1.25 g of $NaNO_3$ was added gradually. The solution was stirred vigorously at 0 – 10ºC (in ice-water bath) for one hour. Then, 7.5 g of $KMnO_4$ was slowly added into the solution, to avoid a rapid rise in temperature of the suspension. The temperature of the solution was kept less than 20ºC under a vigorous stirring for one hour. Then, the solution was kept on stirred at room temperature overnight until a brownish color was obtained. The solution was slowly added with 135 ml of DI water and heated up to 60ºC in an oil bath for one hour and was subsequently cooled down to room temperature. The mixing was terminated by adding 25 ml of H_2O_2. After the peroxide treatment, the solution turned from brown to golden yellow color. The solution was filtered and rinsed twice with 400 ml of HCl in order to eliminate the residual metal ions. Lastly, the solution was rinsed three times with DI water to increase the pH approching 5-6. The GO produced was dried at 60ºC in an oven prior to further use [10]. Plate 3.1 and 3.2 shows a mixture of GO before and after the peroxide treatment.

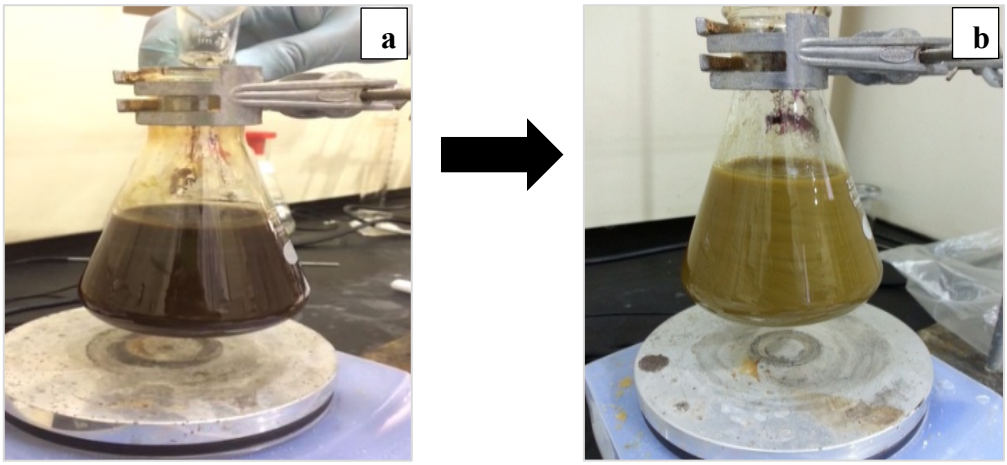

Plate 1: Picture of GO before (a) and after (b) the peroxide treatment

2.3 Modification of Graphene Oxide–Zinc Oxide (GO/ZnO)

A 1 g of GO was taken separately in an Erlenmeyer flasks and sonicated at least for an hour in water phase for a complete dispersion. A mixture of 1g of ZnO was added to the well dispersion of GO and sonicated again for 1 hour at 45ºC. The precipitated GO/ZnO mixture was dried at 60–65ºC inside an oven. Finally, the mixture was crushed in a powder form [12]. The experiment was repeated by varying the ratio of GO to ZnO which are 1:5, 5:5, and 5:1. Meanwhile, the synthesis time of GO-MO was varied under sonication conditions that take up to 30, 60 and 90 minutes. Lastly, the synthesis temperature during sonication was varied to 30, 45 and 60ºC.

2.4 Batch Experiment of Fluoride Removal

The first batch experiment was carried out by adding 0.25 g of GO/ZnO adsorbent to 200 mL of 30mg/L of NaF solution in a conical flask which was kept in a shaker for 60 minutes. Initial fluoride concentration was maintained at 30 mg/L for all the experiments and the

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mixture was agitated at 200 rpm in a mechanical shaker. The solution was filtered and the residual fluoride concentration was measured using Hach DR 2800 spectrophotometer.

2.5 Spectrophotometer Analysis

The purpose of this equipment is to measure the amount of fluoride concentration in a solution. During this analysis, the success of the experiment for fluoride removal by using the adsorption of GO/ZnO can be seen by the differences in the initial and final concentration. The equipment that was used is the Hach DR 2800 spectrophotometer. The SPADNS reagent needed for this analysis is sodium arsenite. Firstly, 10.0 mL of sample was pipetted into a dry square sample cell and 10.0 mL of deionized water was pipetted into a second dry square sample cell. Then, 2.0 mL of SPADNS reagent was pipetted into each cell. The solution was swirled to mix and waited upon for one-minute for the reaction to be completely mixed. The blank (what?) was inserted into the cell holder with the filled line facing right and the result display was 0.00 mg/L F^-. Lastly, the prepared sample was inserted into the cell holder with the filled line facing right. The concentration results are in unit mg/L. The adsorption capacity of fluoride removal was calculated by using following equations:

$$Qe = \frac{Co - Ct}{m} \quad (1)$$

where Co is initial concentration, Ct is equilibrium concentration, m is weight of the adsorbent and Qe is the amount of fluoride adsorbed at equilibrium.

2.7 FTIR Analysis

The GO/ZnO prepared at different synthesis parameters were analyzed using Fourier Transform Infrared Spectroscopy (FTIR). FTIR was used to acquire data related to surface functional groups available on the surface of the GO/ZnO adsorbent. The GO/ZnO sample was placed into a disk for FTIR scans. The IR absorbance data will be obtained for wavenumbers in the range of 400-4000 cm^{-1} for each sample.

3. RESULTS AND DISCUSSION

The main purpose to conduct this research is to study the effect of synthesis parameters on GO/ZnO adsorbent preparation towards fluoride ion (F^-) removal. There are three synthesis parameters that were studied, which are synthesis temperature, synthesis time and ratio of GO to ZnO. The GO/ZnO adsorbents that were synthesized at different parameters were evaluated for F^- removal. The effect of F^- removal was also related with surface functional groups. Figure 1 illustrates the adsorption capacity of fluoride removal at different synthesis parameters of GO/ZnO adsorbent.

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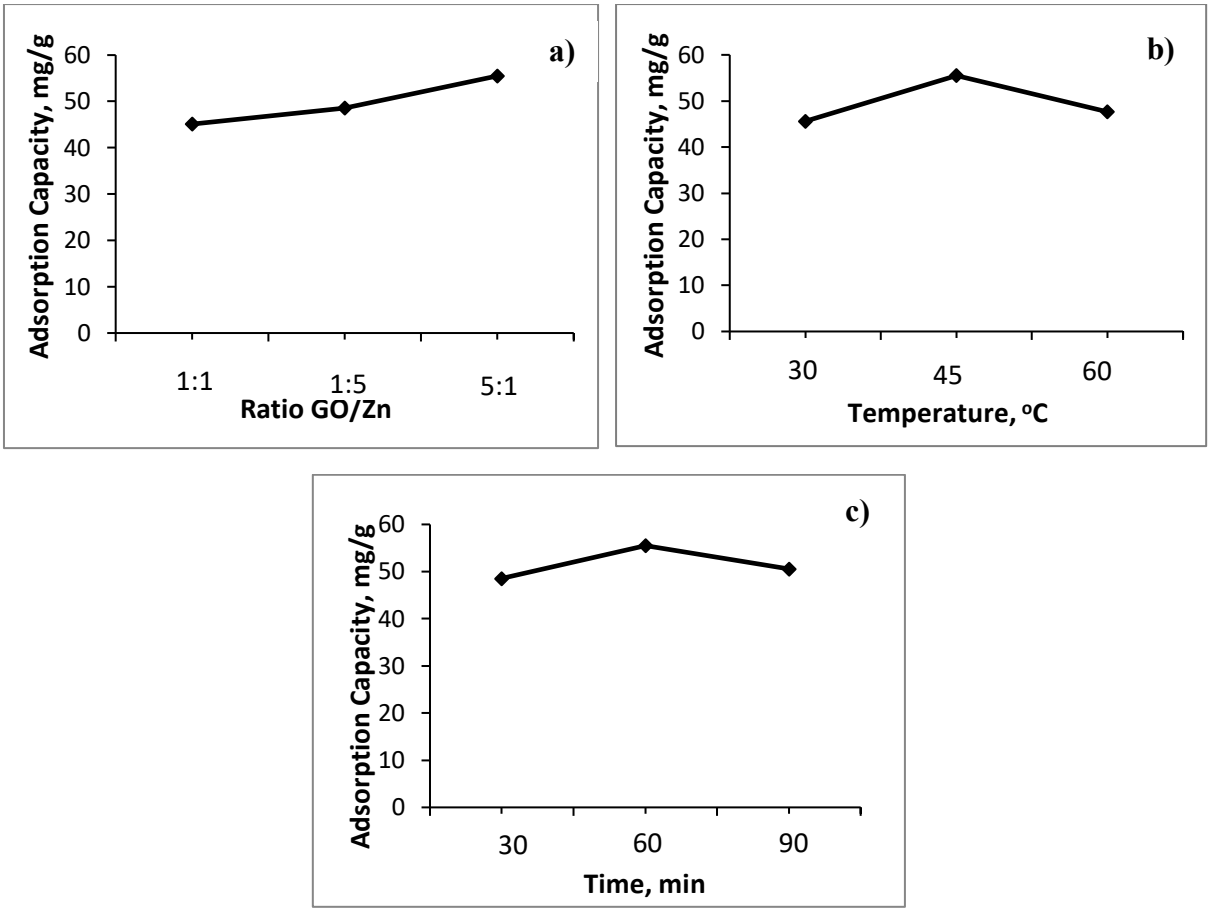

Figure 1: Adsorption capacity of fluoride removal at different synthesis parameters of GO/ZnO adsorbent a) GO/ZnO ratios, b) synthesis temperature and c) synthesis time

3.1 Effect of GO/ZnO Ratio

The ratio of GO to ZnO used in this study are 5:1, 1:5, and 1:1. During the experiment, the synthesis temperature and time were kept constantly at 45°C and 60 minutes, respectively. Based on data in Figure 1(a), ratio 5:1 shows the highest value of fluoride adsorption followed by ratio 1:5 and 1:1, with the value of 55.5 mg/g. This shows the capability of GO/ZnO adsorbent towards the removal of fluoride in wastewater. High fluoride removal is due to high surface area and large adsorption site of GO assisted with the presence of ZnO. The nanostructure of GO contributes to a higher adsorption capacity of fluoride. Hence, the amount of GO needed to mix with ZnO is expected to be greater. GO was investigated based on their potential to adsorb fluoride ion because of its layers and planar structures. Based on previous research, Heidarizad et al. studied on GO/MgO toward the adsorption [12]. The findings showed that the ratio of 5:1 of GO to MgO gave the highest value of methlene blue removal [5]. This is because as the amount of GO increases, the availability of the adsorbent surface area and active sites provided are higher.

3.2 Effect of Synthesis Temperature

The effects of synthesis temperature were varied at 30°C, 45°C and 60°C, while the synthesis time and GO/ZnO were kept constantly for 60 minutes and 5:1 ratio, respectively. Based on data illustrated in Figure 1(b), the adsorption capacity of fluoride was increased to 45°C and

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started to decline at 60ºC. These results show that 45ºC is the desired synthesis temperature for GO/ZnO adsorbent, where high synthesis temperature is not a preference. Low synthesis temperature makes the reaction between GO and ZnO very slow and not effective, while high temperature implies the presence of some residual functional groups and defects [13]. This finding is supported by previous study done by Maab et al. [14], where temperature at 45ºC was selected as an optimum temperature for GO synthesis for fluoride removal. In addition to that, the movements of the molecule in the GO/ZnO solution also contribute towards the outcome of the synthesis. The synthesis of GO/ZnO at low temperature (30°C) will produce low energy molecules, hence resulting in a weak vibration among the molecules. In contra, at high temperature (60°C), the energy of the molecules received will be extremely high, resulting in excessive vibration in the solution of GO/ZnO. Therefore, the synthesis of GO/ZnO at too low and high temperature was not effective compared to the synthesis temperature at 45°C. Prabhu et al. also found that, the adsorption capacity at 45ºC for GO/Zirconium also gives the highest value for fluoride removal which is 10 mg/g. In fact, increasing the temperature has destroyed the plate shape structure, deforming it into a defragmented shape similar to carbon black [5].

3.3 Effect of Synthesis Time

The synthesis time was varied at 30, 60 and 90 minutes, while the ratio of GO to ZnO and synthesis temperature were kept constantly at 5:1 and 45ºC, respectively. Figure 1(c) shows that the highest fluoride removal was obtained at 60 minutes of GO/ZnO synthesis time. One of the factors that contribute to lower fluoride adsorption at 30 minutes synthesis time is the dispersion of GO and ZnO, where at a short synthesis time, the molecules of GO and ZnO were not well dispersed [15]. Hence, 60 minutes of synthesis time could provide enough time for GO/ZnO molecules for well dispersion. In this research work, sonicator has been used to synthesis the GO/ZnO adsorbent. Sonication has numerous effects, both chemical and physical [16]. Once the ultrasound waves are active, there is an alternating adiabatic compression and rarefaction cycle observed, which resulted in cavitation [17-18]. At certain time exposure, the cavitation could happen, where the formation, growth, and sudden collapse of the micro-bubbles in liquids occurred [18]. Based on the results, 30 minutes of synthesis time is not enough for GO and ZnO to form a new bond into each other, hence resulting in lower removal of fluoride, due to less development of the surface area and chemical functional groups. Whereas, longer duration of sonication process is not effective, because the possibility of sudden collapse for GO and ZnO could happen. These factors are interrelated with each other, where the sonochemistry of the synthesis have an effect on the physical interaction between GO and ZnO, resulting in lower or higher removal of fluoride [16].

3.4 Functional Groups of GO/ZnO at Different Synthesis Parameters

The FTIR analysis was conducted on GO/ZnO adsorbent prepared at different synthesis parameters as shown in Figure 2. After an exfoliation of graphite to GO, FTIR analysis reveals the decomposition of epoxy groups and the simultaneous formation of composites of metal oxide particles (ZnO) within the GO composite. The changes of surface functional groups on GO/ZnO adsorbent are thus anticipated.

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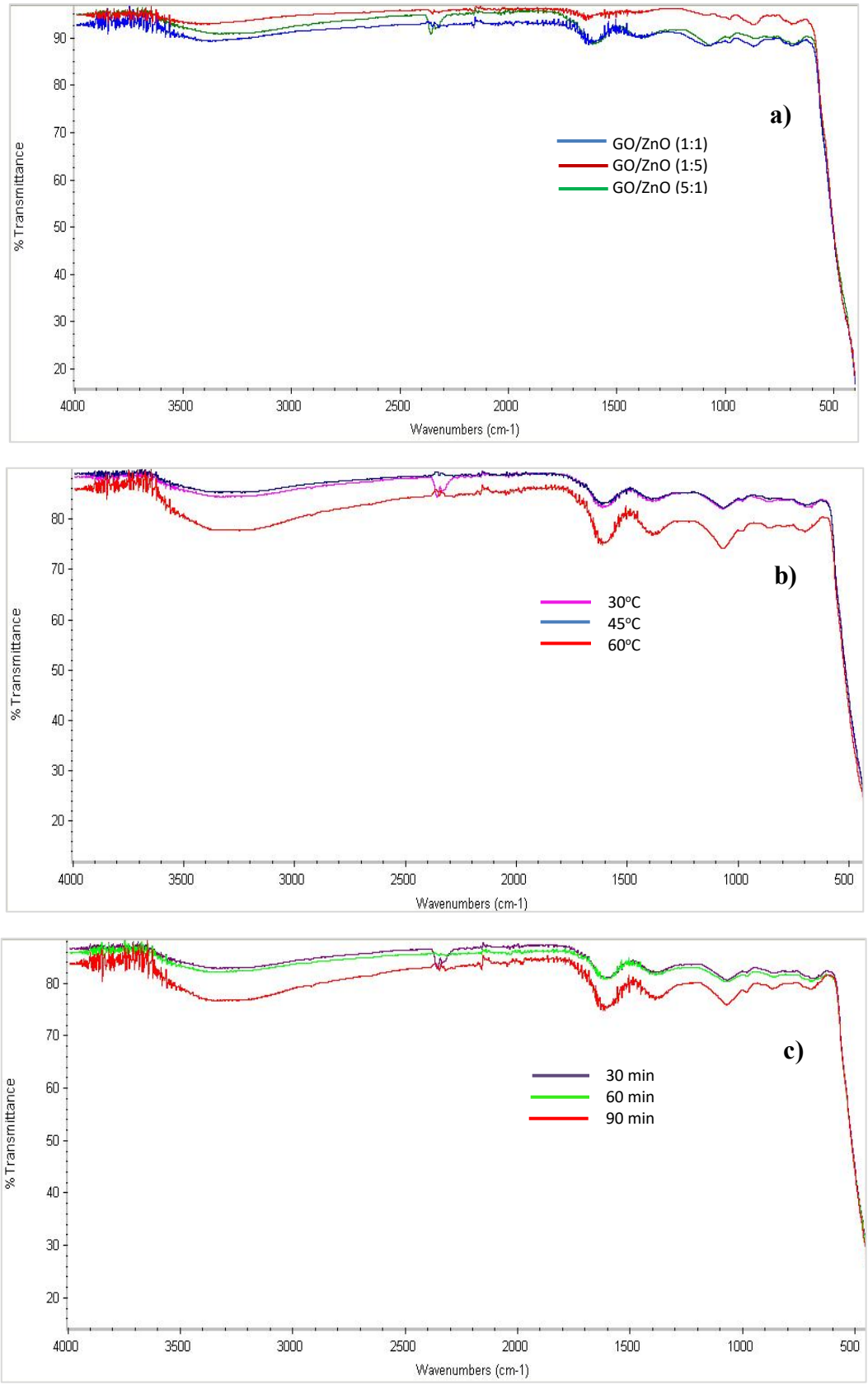

Figure 2: FTIR spectrum of GO/ZnO adsorbent at different synthesis parameters a) GO/ZnO ratio, b) synthesis temperature and c) synthesis time

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From Figure 2, the trends of the spectrum are similar. This is due to the properties and functional group of GO and ZnO. At a peak of 3441 cm^{-1}, it shows that the GO/ZnO adsorbent consists of a hydroxyl group (O-H) and at peak 1760 cm^{-1} shows for C=O group. Meanwhile at a peak 1615 cm^{-1}(what) represents the aromatic group. At a peak of 1403 cm^{-1} and 1221 cm^{-1} what represents the carboxyl (C-O) group and epoxy group, respectively. Lastly, at the peak of 1056 cm^{-1}, it shows an alkoxy group. All the GO/ZnO adsorbent practically has the same active surface functional groups which are in the region of 3500-3950 cm^{-1} [19]. This functional group affects the fluoride adsorption due to the bonding of fluoride ion to the functional group. The intensity or the percentage transmittance is changes where the reaction occurred at the peak. The functional groups involved in the adsorption process are O-H and C-O group. Adsorption capacity relies on upon particles (adsorbate) in liquid diffusing to the surface of a solid (adsorbent), where they bond with the solid surface or are held there by frail intermolecular forces.

4. CONCLUSION

As a conclusion, the synthesis of modified GO with ZnO as an adsorbent for fluoride removal was successfully demonstrated at various synthesis parameters which are synthesis time, synthesis temperature, and GO/ZnO ratio. Various synthesis parameters conducted in the experiments showed that modified GO/ZnO has a potential to become an adsorbent for fluoride removal in wastewater. GO has a rapid equilibrium for the adsorption of fluoride. Based on the result and discussion earlier, there are several condition for synthesis GO/ZnO that gives high adsorption capacity and percentage removal of fluoride. The ratio of GO to ZnO selected is 5:1, the synthesis temperature is 45^{o}C, and lastly for the synthesis time of GO/ZnO is 60 minutes. The best adsorption capacity for fluoride removal was obtained at 55.5 mg/g. The FTIR analysis showed small but significant changes on the peak between the different synthesis parameters. There are no changes in the chemical bond but the intensity or the percentage transmittance is changed due to the reaction that occurred. The difference in percentage transmittance before and after the adsorption process is related to the adsorption capacity.

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